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Characterization of Poly(ether)urethanes

High Resolution Thermogravimetric Analysis

John A. Hiltz
Irvin A. Keough

Defence R&D Canada – Atlantic

Technical Memorandum
DRDC Atlantic TM 2004-023
February 2004

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Abstract

High resolution dynamic mode and stepwise isothermal mode thermogravimetric analysis (TGA) has been used to study the thermal degradation of six thermoplastic poly(ether)urethanes. Poly(ether)urethanes are block copolymers consisting of diisocyanate rich hard segments and poly(ether glycol) rich soft segments. In general, the hardness of these polymers increases with an increase in the percent hard segment in the polymer. The literature indicates that these polymers degrade by a two step mechanism; the diisocyanate rich hard segments in the first step and the poly(ether glycol) rich soft segments in the second step.

The results of the dynamic mode analysis indicated that in general the temperature of the maximum rate of weight loss for the first step (T_{1Max}) decreased as the Shore D hardness of the polymers increased while the temperature of the maximum rate of weight loss for the second step (T_{2Max}) increased as the Shore D hardness of the polymer increased. However, a plot of T_{1Max} against sample Shore D hardness showed considerable scatter. Better correlations were observed when data for the elastomers from a particular manufacturer were considered separately. This suggested that the technique could be sensitive to differences in the morphology of the polymers arising from the synthetic procedure used to prepare them.

The results of the stepwise isothermal mode analysis indicated that the weight losses attributed to the degradation of the hard and soft segments of the polymers correlated well with sample Shore D hardness. That is, the first step weight loss increased as the Shore D hardness increased while the second step weight decreased as the hardness increased. As was observed for the high resolution dynamic analysis, the correlation improved if data for elastomers from a particular manufacturer were considered separately.

Résumé

La dégradation thermique de six poly(éther)uréthanes thermoplastiques a été étudiée par analyse thermogravimétrique (ATG) en mode dynamique haute résolution et en mode isotherme par étape. Les poly(éther)uréthanes sont des copolymères séquencés constitués de segments rigides riches en diisocyanate et de segments tendres riches en poly(éther de glycol). En général, la dureté de ces polymères augmente au fur et à mesure qu'augmente le pourcentage de segments rigides qu'ils renferment. Selon la littérature, ces polymères se dégradent suivant un mécanisme à deux étapes : les segments rigides riches en diisocyanate se dégradent lors de la première étape, tandis que les segments souples riches en poly(éther de glycol) se dégradent lors de la seconde étape.

Les résultats de l'analyse réalisée en mode dynamique indiquaient que, en général, la température à laquelle le taux de perte de poids est maximal au cours de la première étape (T_{1Max}) diminue au fur et à mesure qu'augmente la dureté Shore D, tandis que la température à laquelle le taux de perte de poids est maximal au cours de la seconde étape (T_{2Max}) augmente

au fur et à mesure que s'accroît la dureté Shore D. Toutefois, le graphique représentant T_{1Max} en fonction de la dureté Shore D comportait des points très dispersés. Les corrélations étaient plus étroites lorsque les données relatives aux élastomères d'un fabricant particulier étaient considérées séparément, ce qui permet de penser que cette technique pourrait être sensible aux différences dans la morphologie des polymères découlant du procédé de synthèse utilisé pour les préparer.

Les résultats de l'analyse réalisée en mode isotherme par étape indiquaient qu'il y avait une étroite corrélation entre les pertes de poids attribuables à la dégradation des segments rigides et tendres et la dureté Shore D de l'échantillon. La perte de poids observé lors de la première étape augmentait au fur et à mesure que la dureté Shore D augmentait, tandis que la perte de poids observée lors de la seconde étape diminuait au fur et à mesure que la dureté Shore D augmentait. Comme on l'a observé lors de l'analyse en mode dynamique haute résolution, la corrélation était plus étroite lorsque les données relatives aux élastomères d'un fabricant particulier étaient considérées séparément.

Executive summary

Introduction

Poly(urethanes) are a class of elastomers that are under consideration for a number of defence applications including sound and vibration damping and active vibration isolation. These materials are block copolymers consisting of hard and soft segments. As the percentage hard segment in the polymer changes so do properties such as hardness (modulus) of the polymer. The chemistry of this group of compounds is such that is it possible to prepare a large number of polymers with a broad range of properties. It follows that an understanding of structure/property relationships in the polymers would allow selection and preparation of a polymer with properties optimized (tailored) for an application. An understanding of the structure/property relationships requires analytical techniques to identify polymer structure.

Thermogravimetric analysis (TGA) is a technique where the weight loss of a sample is monitored at constant temperature or as temperature is scanned. It is known that plastic poly(ether)urethanes degrade by a two step mechanism and therefore if the degradation steps can be resolved information on the structure can be derived. In this memorandum, the applicability of two high resolution thermogravimetric analysis modes, high resolution dynamic and stepwise isothermal, to the determination of the structure of these polymers are investigated.

Results

The results of the high resolution dynamic mode TGA indicate that this technique is sensitive to the structure of these compounds. The temperature of the rate of maximum weight loss for the first and second weight loss steps varied with the hardness of the samples. Further, the technique was sensitive to differences in the structures of compounds made by different synthetic techniques.

The results of stepwise isothermal mode TGA indicate that the weight losses for the two degradation steps are related to the hardness of the samples. That is the weight loss attributable to the first step in the thermal degradation process increases as the hardness of the sample increases. Conversely, the weight loss due to the second step of the degradation process decreases as the hardness of the sample increases. Again the technique is sensitive to differences in the structure of compounds made by different synthetic techniques.

Significance

High resolution TGA is a technique that will be used to characteristic polyurethane elastomers proposed for defence applications. The results from this technique will allow a more complete characterization of materials and therefore aid in the material selection process.

Future plans

This technique will be used to study a series of polyurethanes prepared as part of a polymer modelling study. In particular, high resolution TGA will be used to study the ratio of hard and soft segments in these polymers and compare the ratio to that predicted from the ratios of the starting materials.

Hiltz, John A, Keough, Irvin A. 2004. Characterization of Poly(ether)urethanes – High Resolution Thermogravimetric Analysis. DRDC Atlantic TM 2004-023. Defence R&D Canada – Atlantic.

Sommaire

Introduction

Les po.. (uréthanes) constituent une classe d'élastomères que l'on envisage d'utiliser dans un grand nombre d'applications dans le domaine de la défense, y compris pour l'amortissement du son et des vibrations ainsi que pour l'isolement actif des vibrations. Ces matériaux sont des copolymères séquencés comportant des segments rigides et des segments souples. Tout changement dans le pourcentage de segments rigides d'un polymère s'accompagne d'une modification des propriétés, comme la dureté (module). Étant donné leur chimie, on peut utiliser ce groupe de composés pour préparer un grand nombre de polymères possédant une vaste gamme de propriétés. Ainsi, si on comprend les relations qui existent entre la structure et les propriétés des polymères, on pourra choisir et préparer un polymère possédant des propriétés optimisées (établies sur mesure) pour une application donnée. Pour comprendre les relations structure/propriété, il faut faire appel à des techniques analytiques pour identifier la structure des polymères.

L'analyse thermogravimétrique (ATG) est une technique qui permet de suivre la perte de poids d'un échantillon à une température constante ou en fonction d'une variation de température. On sait que les poly(éther)uréthanes thermoplastiques se dégradent suivant un mécanisme à deux étapes; ainsi, on peut obtenir des données sur la structure en suivant les différentes étapes de la dégradation. Dans le présent résumé, on étudie dans quelle mesure deux modes d'analyse thermogravimérique haute résolution, soit l'analyse en mode dynamique haute résolution et l'analyse en mode isotherme par étape, peuvent être appliqués à la détermination de la structure de ces polymères.

Resultats

Les résultats de l'analyse thermogravimétrique réalisée en mode dynamique haute résolution indiquaient que cette technique est sensible à la structure des polymères. La température à laquelle le taux de perte de poids est maximal au cours de la première et de la seconde étape variait avec la dureté des échantillons. De plus, cette technique était sensible aux différences dans la structure de composés préparés grâce à des techniques de synthèse différentes.

Les résultats de l'analyse thermogravimétrique réalisée en mode isotherme par étape indiquaient que la perte de poids lors des deux étapes de dégradation est fonction de la dureté des échantillons. Autrement dit, la perte de poids qui survient au cours de la première étape de la dégradation thermique augmente au fur et à mesure que la dureté augmente. Inversement, la perte de poids attribuable à la seconde étape diminue au fur et à mesure qu'augmente la dureté de l'échantillon. Ici encore, cette technique est sensible aux différences dans la structure de composés préparés grâce à des techniques de synthèse différentes.

Portée

L'analyse thermogravimétrique haute résolution est une technique qui sera utilisée pour caractériser les élastomères à base de polyuréthanes que l'on se propose d'utiliser dans des applications dans le domaine de la défense. Cette technique permettra de procéder à une caractérisation plus complète des matériaux, ce qui aidera quand viendra le temps de faire le choix d'un matériau.

Recherches futures

Cette technique sera utilisée pour étudier une série de polyuréthanes préparés dans le cadre d'une étude de modélisation des polymères, plus particulièrement, pour déterminer le rapport segments rigides/segments tendres et pour comparer ce rapport à celui prévu pour les dans les matériaux de départ.

HILTZ, John A. et KEOUGH , Irvin A. *Caractérisation de poly(étherjuréthanes – analyse thermogravimétrique haute résolution*. RDDC Atlantique TM 2004-023. R &t D pour la défense – Atlantique, 2004.

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1. Introduction

Conventional thermogravimetric analysis instrumentation is used to study the thermal stability/degradation of polymeric materials. In a typical experiment, the sample temperature is increased at a constant rate and the weight loss of the sample measured. For materials with multiple degradation steps, the temperature at which a particular degradation initiates and the temperature range over which the degradation takes place are different for the various steps. The resolution, that is the ability to differentiate between degradation steps, can be improved by slowing the heating rate. However, this increases the analysis time substantially.

Improved resolution and reduced analysis times can be achieved with high resolution thermogravimetric analysis. High resolution thermogravimetric analysis can be carried out in one of two ways. In the first, referred to as the high resolution dynamic mode, the sample is rapidly heated at a set rate until a predetermined rate of weight loss is achieved. The heating rate is then slowed to maintain the predetermined rate of weight loss. When the rate of weight loss falls below a second predetermined level, the heating rate is increased to the set rate again. This is continued until the thermal degradation is complete. In the second, referred to as the stepwise isothermal mode, the sample is rapidly heated at a set rate until a predetermined rate of weight loss is achieved. The temperature is held constant until the rate of weight loss falls below a predetermined rate. Heating is then resumed until the rate of weight loss reaches the predetermined rate. The temperature is held constant until the rate of weight loss drops below the predetermined rate.

Thermoplastic poly(ether)urethanes are segmented A-B block copolymers. They consist of diisocyanate/diol rich hard segments and poly(ether glycol) rich soft segments. The hard and soft segments are thermodynamically incompatible and tend to phase separate. The ratio of the hard and soft segments and their degree of phase separation are critical in determining the properties of poly(ether)urethanes. For instance, the hardness of poly(ether)urethanes is found to increase as the ratio of hard to soft segments increases[1].

In this paper the thermal degradation of six commercial poly(ether)urethanes is studied using high resolution dynamic mode TGA and stepwise isothermal mode TGA.
Poly(ether)urethanes thermally degrade by a two step mechanism[2,3]. In the first degradation step the isocyanate rich hard segments degrade while in the second degradation step the polyether or polyester rich soft segments degrade. It has been noted[3,4] that the temperature at which the first degradation step takes place varies with the ratio of hard and soft segments in the polyurethane. More precisely, the temperature at which the first degradation step starts decreases as the hard to soft segment ratio increases. In addition, the temperature at which the maximum rate of weight loss takes place for the first step increases as the ratio of the soft to hard segments in the polyurethane increases and the temperature of the maximum rate of weight loss for the second step decreases as the ratio soft to hard segments increases.

The high resolution dynamic mode results are discussed with respect to parameters that can be used to differentiate between poly(ether)urethanes containing varying levels of hard and soft segments. These parameters include the temperatures of the maximum rates of weight loss for the two major weight loss steps and the temperature at which the polyurethanes start to

thermally degrade. The stepwise isothermal results are evaluated to determine if weight loss in the two major weight degradation steps for these compounds correlate with hardness of the compounds and therefore the ratio of hard and soft segments in the polymers.

2. Experimental

2.1 Materials

Six commercial poly(ether)urethane thermoplastic elastomers, Texin 990A, Texin 950D, and Texin 970D (Bayer Polymers, Etobicoke, Ontario), Elastollan 1195A and Elastollan 1164D (BASF Corporation-Polymers, Wyandotte, Michigan), and Estane 58300 (B. F. Goodrich, Cleveland, Ohio), were acquired for analysis. The Shore type A or Shore type D Durometer hardness of the six thermoplastic elastomers is shown in Table 1. Equivalent Shore D hardness values are included in Table 1 for those samples supplied with Shore A hardness values.

Previous work[5,6] indicated that the six polyurethanes were methylenebis-(phenylisocyanate) (MDI)/1,4-butanediol (BDO)/poly(tetramethylene ether glycol) (PTMO)-based poly(ether)urethanes.

Table 1. Shore Type A and/or Shore Type D hardness of the six poly(ether)urethanes.

SAMPLE	MANUFACTURER	SHORE HARDNESS
Texin 990A	Bayer Polymers	90A/39D
Texin 950D	Bayer Polymers	50D
Texin 970D	Bayer Polymers	70D
Elastollan 1195A	BASF Plastics	95A/46D
Elastollan 1164D	BASF Plastics	64D
Estane 58300	B. F. Goodrich	80A/29D
The table footnote – Equivalent Shore D hardness values for Shore A hardness values were supplied by Shore Instrument Company, Freeport, Long Island, New York.		

2.2 Thermogravimetric Analysis

Thermogravimetric analysis was carried out on a model Q500 thermogravimetric analyser (TA Instruments, New Castle, Delaware). The apparatus was temperature calibrated using a Nickel standard. All analyses were carried out in platinum sample pans. Nitrogen was used as the balance and sample gas at flow rates of 40.0 mL/min and 60 mL/min respectively. Two temperature program modes, high resolution dynamic and stepwise isothermal, were used.

Five analysis were carried out on each of the six poly(ether)urethanes in the high resolution dynamic mode. The sensitivity was 1.0 (range 1.0 to 8.0) and the resolution was 4 (range 0 to 8). The sensitivity determines how much of a change in the baseline is seen as a weight loss by the instrument. The resolution determines how much the heating rate is slowed once a weight loss is detected. The heating rate was 50.0 °C/min when no weight loss was detected.

One analysis of each of the six poly(ether)urethanes was carried out in the stepwise isothermal mode. The heating rate was 20.0 °C/min until the rate of weight loss exceeded 1.0%/min. At this point the temperature was held constant until the rate of weight loss fell below 0.1%/min. The heating rate was then increased to 20 °C/min until the rate of weight loss exceeded 1.0%/min.

2.3 Statistical Analysis

An analysis of variance was carried out on the high resolution dynamic mode data to determine if differences in measured parameters for the six samples were significant (caused by differences in the sample composition, for instance) and therefore could be used to distinguish between the samples[7,8].

In this analysis it is assumed that the results for each of the six samples arise from six normally distributed populations with the same variance and with means $\mu_1, \mu_2, \ldots \mu_6$. The hypothesis that the means are equal is tested.

Analysis of variance involves decomposition of the 'sum of squares', q, into two parts q_1 and q_2 where q_1 results from the variation between the groups and q_2 results from the variation within the groups. The two parts are then compared to determine if the hypothesis is true.

$$q = \sum_{i=1}^{r} \sum_{k=1}^{n} (x_{ik} - \bar{x})^2 \qquad (1)$$

$$q = q_1 + q_2$$

The two parts of the sum of squares, q_1 and q_2 were calculated using equation (2) where x_{ik} represents the result from the i^{th} row and k^{th} column.

$$g_i = \sum_{k=1}^{n_i} x_{ik}$$

$$g = g_1 + g_2 + ... + g_r$$

$$g = g^2$$

$$u = \sum_{i=1}^{r} \sum_{k=1}^{n_i} x_{ik}^2 \qquad (2)$$

$$q = u - g$$

$$q_1 = g_1^2 / n_1 + g_2^2 / n_2 + ... + g_r^2 - g$$

$$q_2 = q - q_1$$

In this study there were six poly(ether)urethanes and each was analysed five times using the high resolution dynamic mode. For r=6 groups and n=30 results the quotient v_o is calculated where r-1 (5) and n-r (24) represent the degrees of freedom between the groups and between the individual data points respectively.

$$v_o = \frac{q_1 /(r-1)}{q_2 /(n-r)} \qquad (2)$$

A significance level (α) for the result is then selected, in this case 5%, and the solution c of the equation $P(v_o \leq c) = 1 - \alpha$ taken from a F-distribution table for 5 and 24 degrees of freedom. If $v_o \leq c$ then we do not reject the hypothesis that the means are equal.

3. Results and Discussion

3.1 High Resolution Dynamic TGA

The results of a high resolution dynamic TGA of a sample of Texin 950D are shown in Figure 1. The thermogram includes plots of weight % (wt %) versus temperature (T) and the derivative of wt % with respect to T (d(wt%)/dT) versus T. Although the plot of wt% against T shows two weight loss steps, between approximately 285°C and 345°C and 345°C and 400°C, the two steps are more readily seen in the plot of d(wt%)/dT versus T. The maxima in the d(wt%)/dT versus T plots, at 299.71°C (T_{1Max}) and 377.25°C (T_{2Max}), are marked in Figure 1 along with the temperature at which the sample starts to degrade 294.67°C (T_i).

Plots of d(wt%)/dT versus T for the Texin 990A, Texin 950D, and Texin 970D are shown in Figure 2. It should be noted that these are plots of one of five runs for each of these samples. For these runs, T_{1Max} increased as the hardness of the samples decreased. T_{2Max} was similar for Texin 990A and Texin 950D and increased for Texin 970D for these runs.

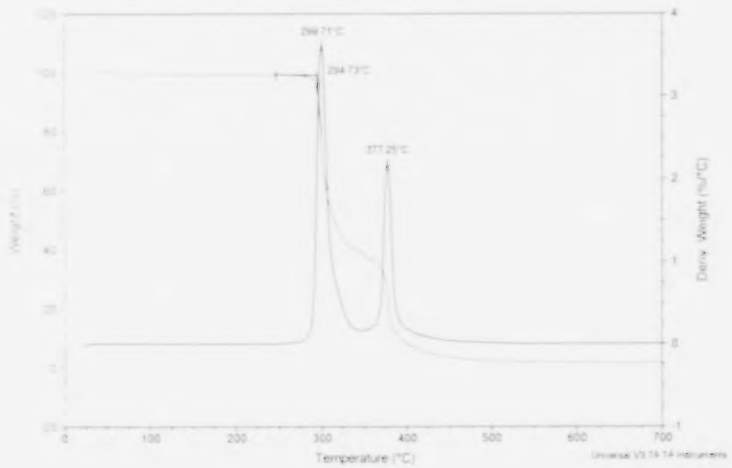

Figure 1. Thermogram of Texin 950D showing plots of %wt versus T and d(%wt)/dT) versus T.

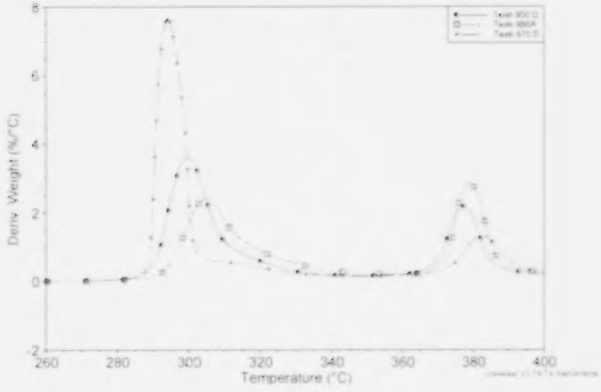

Figure 2. Plots of d(wt%)/dT versus T for Texin 990A, Texin 950D and Texin 970D

Plots of d(wt%)/dT versus T for the Elastollan 1195A, Elastollan 1164D and Estane 58300 samples are shown in Figure 3. As was noted for the Texin samples, these are plots of one of five runs for each of the samples. T_{1Max} increased as the hardness of the samples decreased for the Elastollan samples. T_{1Max} for Estane 58300 fell between that for the two Elastollan samples even though its hardness was less than the Elastollan 1195A sample. T_{2Max} increased as the hardness of the samples increased.

The T_{1Max} data for the six polyurethanes are shown in Table 2. A plot of the average T_{1Max} values versus Shore D hardness is shown in Figure 4. There is considerable scatter in this plot. However, if the points for the Texin samples are considered separately, T_{1Max} decreases monotonically with an increase in the Shore D hardness. Similarly, T_{1Max} of the Elastollan samples decreases with an increase in the Shore D hardness. However, the T_{1Max} temperatures for the Elastollan samples are higher than would be predicted from the plot of T_{1Max} against hardness for the Texin samples. This suggests that something other than the hardness (ratio of hard to soft segments) is affecting the temperature of maximum rate of weight loss.

Differential scanning calorimetry[5] indicated that the Elastollan samples had a higher level of phase separation and microcrystallinity in the hard segments than the Texin samples with similar hardness values. It was postulated that this was due to differences in the average length of the hard segments in the Texin and Elastollan samples. The synthetic procedure used to prepare these polyurethanes, that is, a one or a two step synthesis is known to affect the average length of the hard segment[9]. The increased thermal stability of the hard segments in the Elastollan samples would be consistent with higher molecular weight, phase separated,

microcrytalline urethane rich hard segments[5] in the Elastollan samples compared to the Texin samples.

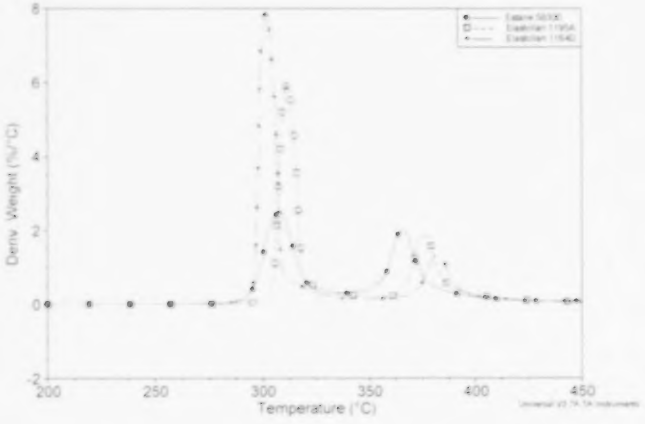

Figure 3. Plots of d(wt%)/dT versus T for Elastollan 1195A, Elastollan 1164D, and Estane 58300.

An analysis of variance was carried out to determine the average T_{1Max} values for the six polyurethane samples were significantly different. The critical value of v_o (c) for 5 and 24 degrees of freedom and a 95% confidence level was 2.62. The v_o calculated for the T_{1Max} data was 12.33 indicating that the average T_{1Max} values were not from the same population and were therefore significantly different.

The T_{2Max} data for the six polyurethane samples are shown in Table 3. A plot of the average T_{2Max} values versus Shore D hardness is shown in Figure 5. In general, T_{2Max} values increase as the hardness of the samples increases. This is in agreement with the literature[1,2]. Unlike the T_{1Max} versus hardness plot, the data for the Texin and Elastollan samples fall on the same 'line', with the exception of the point for the Texin 990A sample. It has been observed that the stability of the soft segments in MDI/BDO/PTMO-based poly(ether)urethanes increase as the molecular weight of the PTMO used in their preparation increases[2]. As the T_{2Max} for the Texin 990A is higher than would be predicted based on the other samples, this may be due to the molecular weight of the poly(ether glycol) used to prepare this sample being higher than that for the other samples.

An analysis of variance calculation was carried out to determine if the average T_{2Max} values for the six samples were significantly different. The value of c for 5 and 24 degrees of

freedom and a 95% confidence level was 2.62. The value of v_o was calculated to be 20.89, indicating that the average T_{2Max} values were not from the same population and were therefore significantly different.

The T_i data for the six polyurethane samples are shown in Table 4. A plot of the average T_i value against Shore D hardness is shown in Figure 6. As was observed for the plot of T_{1Max} against Shore D hardness there was considerable scatter in the plot. For the Texin samples, T_i decreased in going from Texin 990A to Texin 950D but then increased slightly for Texin 970D. T_i decreased in going from Elastollan 1195A to Elastollan 1164D. As was observed for T_{1Max} values, the T_i values for the Elastollan samples were higher than would be predicted from the Texin 990A, Texin 950D and Estane 58300 data. In addition the result for Texin 970D falls closer to the 'line' defined by the Elastollan data than for the other Texin samples and Estane 58300.

Two factors appear to be affecting T_i. One is the percent hard segment in the elastomers and the second the degree of phase separation and microcrystallinity in the in the elastomers resulting from the method used to synthesize them.

An analysis of variance calculation was carried out to determine if the average T_i values for the six samples were significantly different. For 5 and 24 degrees of freedom and a 95% confidence level, c was 2.62. For the data v_o was 14.31 indicating that the average T_i values were not from the same population and were therefore significantly different.

Table 2. T_{1Max} data from five high resolution dynamic TGA runs for six poly(ether)urethanes.

RUN	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	AVERAGE
SAMPLE	T_{1max} (°C)					
Texin 990A	301.5	306.8	304.9	301.7	296.1	302.2
Texin 950D	301.3	297.5	299.7	296.7	294.2	297.9
Texin 970D	297.8	295.0	294.0	293.6	294.7	295.0
Elastollan 1195A	310.8	309.8	310.8	305.8	305.6	308.5
Elastollan1164D	296.4	297.7	301.5	308.2	299.9	300.7
Estane 58300	307.3	301.6	307.8	310.8	308.7	307.3
Analysis of variance – c for 5 and 24 degrees of freedom and a 95% confidence level was 2.62. v_o for the data was 12.33 indicating that the average T_{1Max} values were not from the same population and were therefore significantly different.						

Table 3. T_{2Max} data from five high resolution dynamic TGA runs for six poly(ether)urethanes.

RUN	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	AVERAGE
SAMPLE	T_{2max} (°C)					
Texin 990A	381.2	372.8	378.9	377.4	371.7	376.4
Texin 950D	377.5	373.7	377.1	377.7	373.8	376.0
Texin 970D	384.8	383.3	382.4	378.8	383.9	382.4
Elastollan 1195A	376.8	375.8	375.5	371.9	371.7	374.3
Elastollan1164D	377.0	377.7	382.1	380.0	377.3	378.8
Estane 58300	369.7	365.2	365.6	365.2	367.6	366.7

Analysis of variance – c for 5 and 24 degrees of freedom and a 95% confidence level was 2.62. v_o for the data was 20.89 indicating that the average T_{2Max} values were not from the same population and were therefore significantly different.

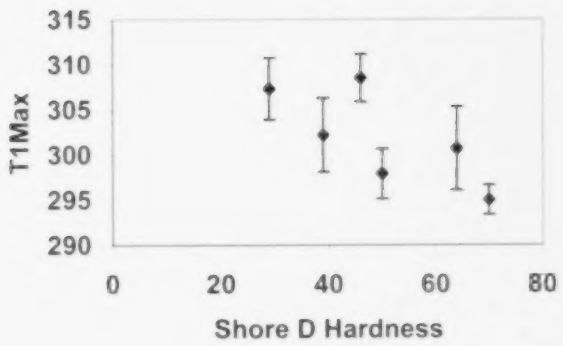

Figure 4. Plot of T_{1Max} against Shore D hardness for the six poly(ether)urethanes.

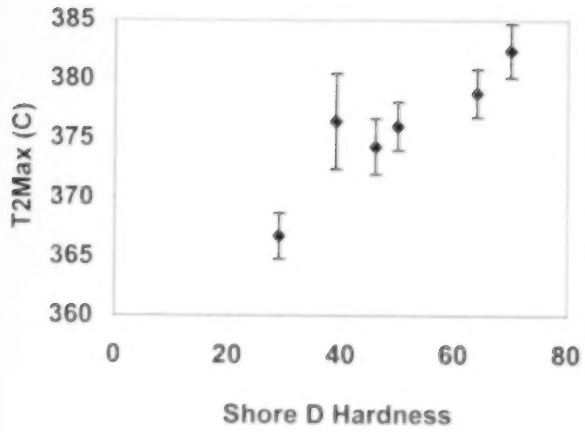

Figure 5. Plot of T_{2Max} against Shore D hardness for the six poly(ether)urethanes.

Table 4. T_i data from five high resolution dynamic TGA runs for the six poly(ether)urethanes.

SAMPLE/RUN	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	AVERAGE
	T_i (°C)					
Texin 990A	296.2	299.4	298.4	295.0	292.3	296.2
Texin 950D	293.0	294.0	294.1	295.8	290.2	293.4
Texin 970D	295.5	294.7	293.7	293.2	292.3	293.9
Elastollan 1195A	307.9	306.4	309.8	302.8	303.3	306.0
Elastollan1164D	297.2	297.3	300.7	306.4	299.8	300.3
Estane 58300	305.2	299.3	299.8	309.2	300.9	302.9

Analysis of variance – c for 5 and 24 degrees of freedom and a 95% confidence level was 2.62. v_o for the data was 14.31 indicating that the average T_{2Max} values were not from the same population and were therefore significantly different.

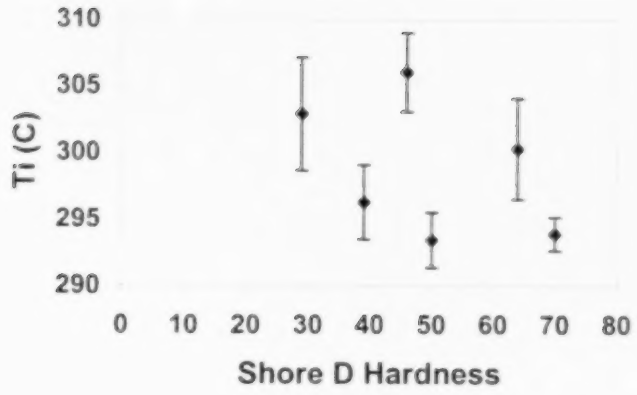

Figure 6. Plot of T_i against Shore D hardness for the six poly(ether)urethanes.

3.2 Stepwise Isothermal Thermogravimetric Analysis

A stepwise isothermal TGA trace (thermogram) for Texin 950D is shown in Figure 7. Four distinct weight loss steps were observed for this sample. These are labelled in Figure 7 as steps 1 through 4. The weight losses for steps 1 and 2 are attributed to the degradation of the urethane rich hard segments and the poly(ether glycol) rich soft segments of these poly(ether)urethanes. The weight losses in Steps 3 and 4 result from the loss of more stable material, possible arising from the degradations in Steps 1 and 2.

Four distinct weight loss steps were also observed in the stepwise isothermal degradation of the other poly(ether)urethanes. The weight losses for each of the degradation steps for the six poly(ether)urethane samples are shown in Table 6. The losses were normalized to the total weight loss for the four steps. That is weight loss up to ~250°C and weight remaining above ~800°C were ignored.

An overlay of the stepwise isothermal thermograms of the six samples is shown in Figure 8. Comparison of the percent weight losses for the first degradation steps of the six samples indicates that they increase as the hardness of the samples increase. Conversely, the weight losses in the second steps decrease as the hardness of the samples increase. A plot of the step 1 weight loss (%HS) and step 2 weight loss (%SS) for the six samples is shown Figure 9.

These results indicate for a series of poly(ether)urethanes synthesized from the same diisocyanate, diol and poly(ether glycol) that the percent hard segment correlates with sample hardness. As sample hardness is related to the percent hard segment in poly(ether)urethanes

this technique is applicable to the determination of hard and soft segment concentration in poly(ether)urethanes of unknown composition.

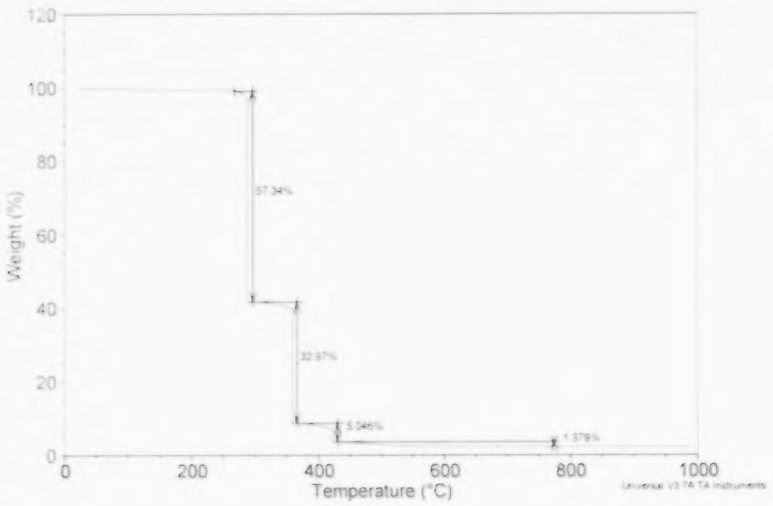

Figure 7. Stepwise isothermal plot of wt% against T for Texin 950D. The four weight loss steps are indicated on the plot.

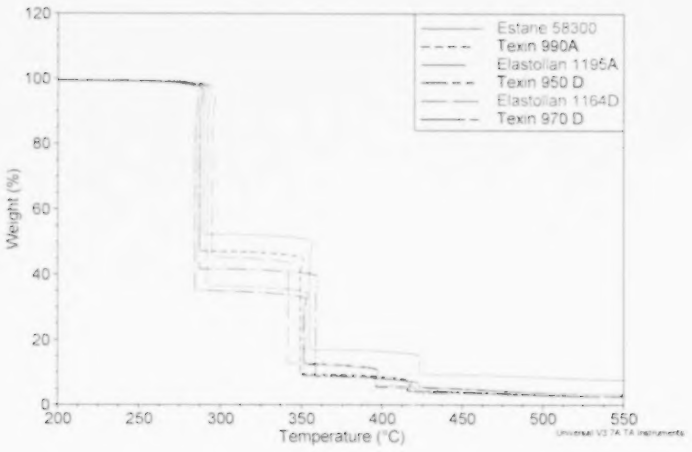

Figure 8. Stepwise isothermal plots for the six poly(ether)urethanes.

Table 5. Percent weight loss for steps in stepwise isothermal TGA analysis.

SAMPLE/ % WT LOSS	STEP 1	STEP 2	STEP3	STEP4
Texin 990A	53.63	39.00	5.39	1.97
Texin 950D	59.26	34.02	5.27	1.45
Texin 970D	65.91	26.96	4.96	2.17
Elastollan 1195A	56.03	33.78	7.69	2.49
Elastollan1164D	65.11	25.13	6.75	3.01
Estane 58300	50.88	38.11	8.27	2.74

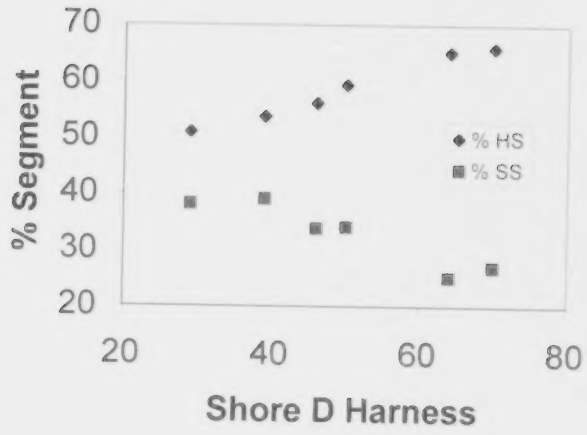

Figure 9. Plot of weight percent hard segment (% HS) or soft segment (% SS) against Shore D hardness for the six poly(ether)urethanes.

4. Conclusions

A series of six poly(ether)urethanes have been characterized using high resolution TGA. The results of high resolution dynamic experiments indicate that the technique is sensitive to differences in the percent hard and soft segments in the sample and the polymer microstructure. That is, the temperature of the maximum rate of weight loss for the first degradation step (T_{1Max}) decreases as the percent hard segment in the polymer increases. Conversely, the temperature of the maximum rate of weight loss for the second degradation step (T_{2Max}) decreases as the percent hard segment in the polymer increases. T_{1Max} was also found to depend on the microstructure (average molecular weight of the hard segments) of these phase separated polymers. That is, the correlation between sample hardness and T_{1Max} was different for the Texin and Elastollan samples.

The results of stepwise isothermal analysis indicate that the weight losses attributable to hard and soft segment thermal degradation steps correlate with sample hardness. More specifically, the percent weight loss due to the urethane rich hard segment increases as the hardness of the sample increases while the percent weight loss due the soft segment decreases as the sample hardness increases. This should be a useful analytical tool for the characterization of synthesized polyurethanes. For instance, this will allow comparison of the actual percent hard and soft segments in a polymer to that predicted by the reaction stoichiometry.

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High resolution dynamic mode and stepwise isothermal mode thermogravimetric analysis (TGA) has been used to study the thermal degradation of six thermoplastic poly(ether)urethanes. Poly(ether)urethanes are block copolymers consisting of diisocyanate rich hard segments and poly(ether glycol) rich soft segments. In general, the hardness of these polymers increases with an increase in the percent hard segment in the polymer. The literature indicates that these polymers degrade by a two step mechanism; the diisocyanate rich hard segments in the first step and the poly(ether glycol) rich soft segments in the second step.

The results of the dynamic mode analysis indicated that in general the temperature of the maximum rate of weight loss for the first step (T_{1Max}) decreased as the Shore D hardness of the polymers increased while the temperature of the maximum rate of weight loss for the second step (T_{2Max}) increased as the Shore D hardness of the polymer increased. However, a plot of T_{1Max} against sample Shore D hardness showed considerable scatter. Better correlations were observed when data for the elastomers from a particular manufacturer were considered separately. This suggested that the technique could be sensitive to differences in the morphology of the polymers arising from the synthetic procedure used to prepare them.

The results of the stepwise isothermal mode analysis indicated that the weight losses attributed to the degradation of the hard and soft segments of the polymers correlated well with sample Shore D hardness. That is, the first step weight loss increased as the Shore D hardness increased while the second step weight decreased as the hardness increased. As was observed for the high resolution dynamic analysis, the correlation improved if data for elastomers from a particular manufacturer were considered separately.

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